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Application of Interfacial Polymerization upon Wool

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Comparative studies have been made of three types of treatments which utilize diisocyanates for stabilization of wool yarns and fabrics, and it has been shown that the procedures which utilize the technique of interfacial polymerization as developed by Whitfield et al. is most effective. The procedures of interfacial formation of polyurea upon fiber surface were studied in detail, and it was found that the employment of ethylene diamine, which had not hitherto been used as a diamine component, resulted in the best shrinkproof effect. The electron microscopic study revealed that the fibers treated by this procedure were masked uniformly by the polyurea resin. The conditions of treatment were varied, and the influence of these conditions upon the uptake and shrinkproof effect was studied. The uptake of from 2 to 5% was sufficient to make the yarns and fabrics practically unshrinkable. The mechanical properties and the moisture regain of the fibers were not significantly affected by the treatment. The anti-scale coefficient of friction decreased by the treatment, and therefore the directional frictional effect decreased. This would be the main factor of producing the shrinkproof effect.

INTRODUCTION

A series of developing works has been done by Whitfield, Miller and Wasley^{1,2,3,4)} for securing wool fabric stabilization by interfacial polymerization. Their study is very comprehensive and covers almost all the possibilities of interfacial formation of polymers upon wool, such as polyamides, polyurethanes, polyureas, polyesters and polycarbonates, employing varieties of components for polymer formation. According to them there are a number of procedures that are very effective for making wool fabrics shrink resistant without producing significant alteration of handle. Most of the reactions that are utilized by them are the polycondensation reactions which liberate hydrochloric acid at polymer formation. Whereas, the reactions of diisocyanates with diamines lead to the formation of polyureas without liberating any other reaction products, on which, however, only a brief description has been made by them. We have also taken an interest in making polyureas interfacially upon wool fibers from the stand point that the procedure will not liberate hydrochloric acid which might affect the wool fibers, and have made a series of experiments in detail, and compared the results with respect to wool fabric stabilization with those obtained by other procedures which use isocyanates as reagents.

There have been a series of studies published on the application of

* 堀尾 正雄, 船津 実, 近土 隆, 関本 健一

monofunctional, difunctional and polyfunctional isocyanates upon wool fibers and fabrics. Farnworth⁵⁾, Moore⁶⁾, and Moore and O'Connell⁷⁾ modified wool by treating it with isocyanates in pyridine, and found that its increasing uptake reduced the felting shrinkage and imparted stability to the material subject to degradation by alkali and oxidizing and reducing agents. Later Koenig improved the method by treating the wool fabrics in the presence of hot dimethyl sulfoxide⁸⁾ and dimethyl formamide⁹⁾. The 19 aromatic and aliphatic monoisocyanates, 6 diisocyanates and 1 polyisocyanate have been used as reagents. The modified fabrics were also found more resistant to laundering shrinkage, but their physical properties were usually poorer than those of the untreated fabric. The modification of wool by these procedures is thought to be the result of reactions of isocyanates penetrated into the wool fibers with the functional groups of aminoacids of wool, such as hydroxyl, sulfhydryl, amino and carboxylic groups. In the case of treatment with diisocyanates and polyisocyanates the formation of cross linkages is also possible.

Another type of utilization of diisocyanates as modifying agents of wool originates from the studies made by Barr, Capp and Speakman¹⁰⁾, who attempted to deposit polymers upon the fiber surface. The stabilizing effect was found to be due to the masking of the scale structure of the fiber surface. The diisocyanate is partially converted into diamine by reaction with the absorbed water of wool, and this diamine forms polyurea with the unchanged diisocyanate. The *m*-xylene diisocyanate and hexamethylene diisocyanate were used in various media. The method was further improved by supplying hexamethylene diamine, in addition to the diamines resulting from diisocyanates by hydrolysis. This type of modification was successfully developed by applying the technique of interfacial polymerization by Whitfield et al. as mentioned before. The fabric is immersed in the aqueous solution of the first component, such as diamine, and passed through the squeeze rolls to remove excess solution. Subsequently the fabric is immersed in a non-aqueous solution of the second component, such as diisocyanate, which makes polymer with the first component. The formation of polymer takes place instantaneously at the fiber surface, when the fabric is immersed in the solution of the second component. The order of immersion can be altered, that is—the wool fabric is first treated with the anhydrous solution of diisocyanate, and then with the aqueous solution of diamine. The fabric is finally rinsed thoroughly and dried. Whitfield et al. used methylene-bis-*p*-phenylisocyanate and toluene diisocyanate as the diisocyanate component, and hexamethylene diamine and *m*-xylene diamine as the diamine component. It is found by us that toluene diisocyanate is superior, but the most important point is the fact that ethylene diamine, which has been used by us first, is by far superior to other diamines which have been used heretofore.

COMPARISON BETWEEN SEVERAL PROCEDURES

The methods for stabilization of wool fabrics and yarns utilizing diiso-

cyanates are classified into three types: Type I aims at the reactions of diisocyanates with functional groups of wool. Type II modifies wool by depositing polyurea upon fiber surface by the reaction of diisocyanate and the diamine which is produced from the diisocyanate by hydrolysis. Type III utilizes the interfacial polymerization on the surface of wool fibers. These three types of procedures were compared with each other with respect to shrink-proofing at an uptake (gain in weight) of about 5% by using the toluene diisocyanate (hereafter TDI) as the reagent. The commercial knit yarn of wool was used as a sample, which had been extracted thoroughly in a Soxhlet apparatus with the mixture of benzene-methanol of 1:1 in volume, washed with water and dried at 70°C *in vacuo* for 3 hours, and placed in a desiccator over phosphoric anhydride. About 2 g. of the yarn were subjected to this treatment, and the change in shrinking property was measured.

The Conditions of Treatments

The condition of each type of treatment was as follows:

Type I. 10 ml. of TDI was mixed with 40 ml. of dimethyl sulfoxide, and the yarn was immersed in this medium at 50°C for 6 min., and washed several times with methanol, then with water and dried. The uptake was 5.01%.

Type II. The sample was immersed in 50 ml. of 6% solution of TDI in carbon tetrachloride at 50°C for 10 min., and squeezed up to the solution uptake of 100%. The wet yarn was further immersed in 50 ml. of water at 50°C for 10 min., squeezed and heated up to 90 to 100°C in air for 10 min. and washed with methanol, and then with water, and dried. The uptake of the resin was only 2.00%. The sample is denoted by Type IIa. The procedure was repeated once again with the sample of Type IIa. The uptake increased up to 4.84%. This is denoted by Type IIb.

Type III. The yarn was immersed in 50 ml. of 4% solution of TDI in carbon tetrachloride at room temperature, and squeezed up to the solution pickup of 100%, and this was immersed in 50 ml. of aqueous solution of hexamethylene diamine at 50°C for 5 min. and squeezed, washed with methanol, then with water, and dried. The uptake was 5.89%. This is designated as Type IIIa.

On the other hand, in the procedure designated as Type IIIb, ethylene diamine was used instead of hexamethylene diamine. The other conditions of treatment were the same as those of Type IIIa, except that the concentration of TDI was 6%. The uptake was 5.20%.

The Method of Testing

The sample yarn weighing 2 g. had the length of about 65 cm. The yarn was hung perpendicularly by balancing it with a weight of 2 g. at an end, and marked the length of 60 cm. by an insoluble color, leaving margins at both the ends, which were fixed respectively at the hook fitted at each end of a glass cylinder having a diameter of 2 cm. The distance between the two hooks was 20 cm. The cylinder was poured with water for just half of its

volume, and settled horizontally on a vibrator, which vibrated horizontally with the frequency of 120 cycles per minute with the amplitude of 12 cm. The tests were performed in a conditioned room kept at 20°C. The yarn was taken out of the cylinder after being shaken for a certain time, and dried, and the distance between the marks was measured, hanging the yarn perpendicularly with a weight of 2 g. at an end. The shrinkage of the yarn is expressed by the formula, $100(60-l)/60$, in %, where l is the distance between the marks after shaking.

Results

The results of experiments are shown in Table 1 and Fig. 1.

Table 1. Shrinkage tests of yarn processed by various types of treatments.

Type of treatment	Uptake (Weight increase) %	Shrinkage at various time of shaking, %					
		10 min.	20 min.	30 min.	60 min.	120 min.	180 min.
Untreated		4.7	10.8	16.1	33.0	43.0	43.0
I	5.01	—	—	—	12.5	27.3	38.0
IIa	2.00	—	—	—	6.5	29.3	39.7
IIb	4.84	—	—	—	3.2	11.0	36.4
IIIa	5.89	—	—	—	2.8	4.8	6.8
IIIb	5.20	—	—	—	-0.7	-1.0	-0.8

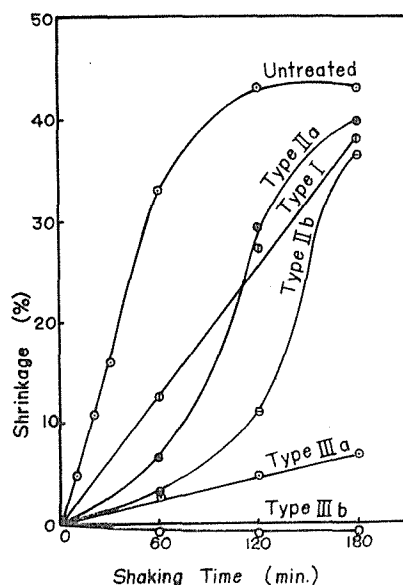


Fig. 1. Shrinkage tests of yarn processed by various types of treatments employing the diisocyanate.

The shrinkage vs. time curve of the untreated yarn reaches the saturation point at the shrinkage of 43.0% under the present condition of experiment.

The yarn treated by the procedure of Type I is more resistant to shrinkage at the short time of vibration, but the shrinkage increases almost linearly with the length of time. The shrinkage after 180 min. of shaking is 38.0%, and is not very small compared to that of the untreated yarn. The same thing applies also to the yarn treated by the procedures of Type II. The shrinkage after 60 min. of shaking is very small, and indeed, the smaller as the uptake is greater. With increased length of time of shaking, however, the resistance to the felt shrinkage drops rapidly, and the slope of shrinkage vs. time curve becomes almost the same as that of the untreated yarn. This would mean that the resin deposited by the procedures of Type II is not so stably fixed upon the fiber surface, but is removed readily during the shaking.

In comparison with the treatments of Type I and II, the procedures of Type III, which utilize the technique of interfacial polymerization, are more effective to enhance the stability of yarns. The procedure of Type IIIa employs hexamethylene diamine as a diamine component, and is on the whole similar to one of the procedures proposed by Whitfield et al., but the similar procedure of Type IIIb, which has been developed by us and employs ethylene diamine as a diamine component, is most effective for securing the dimension stability of the yarn. On the other hand, there is no perceptible difference between the handles of the yarns treated by the procedures of Type IIIa and IIIb.

Electron Microscopic Observations

The electron photomicrographs of the replicas of fiber specimens of the untreated wool and the wool treated by the procedures of Types I, II, and III are shown in Fig. 2, a, b, c and d. The surface of the wool is not affected perceptively by the treatment of Type I, as can be deduced from the comparison between the photomicrographs of Fig. 2, a and b. This is reasonable, for the modification of wool by the procedure of Type I is chiefly due to the chemical reactions of diisocyanate with the functional groups of wool, resulting in the formation of branching and cross-linking.

The deposition of resin on the fiber surface is seen in the photomicrographs of the replicas of fibers treated by the procedure of Type II, as is shown in Fig. 2, c. The surface is not uniformly covered by the resin, but the deposition takes place chiefly at the spaces close to the edges of scales. This is very compatible with the results of the experiments of shrinkage tests, which showed that the resin would be readily removable from the fibers treated by the procedure of Type II.

The photomicrograph of fiber treated by the procedure of Type III is most characteristic, as can be seen in Fig. 2, d. The surface is uniformly covered by the resin, and the scaly structure is almost completely masked.

These electron microscopic observations suggest that the felting shrinkage of yarns and fabrics can be reduced more effectively by the modification of fiber surface than by the chemical modification of wool keratin.

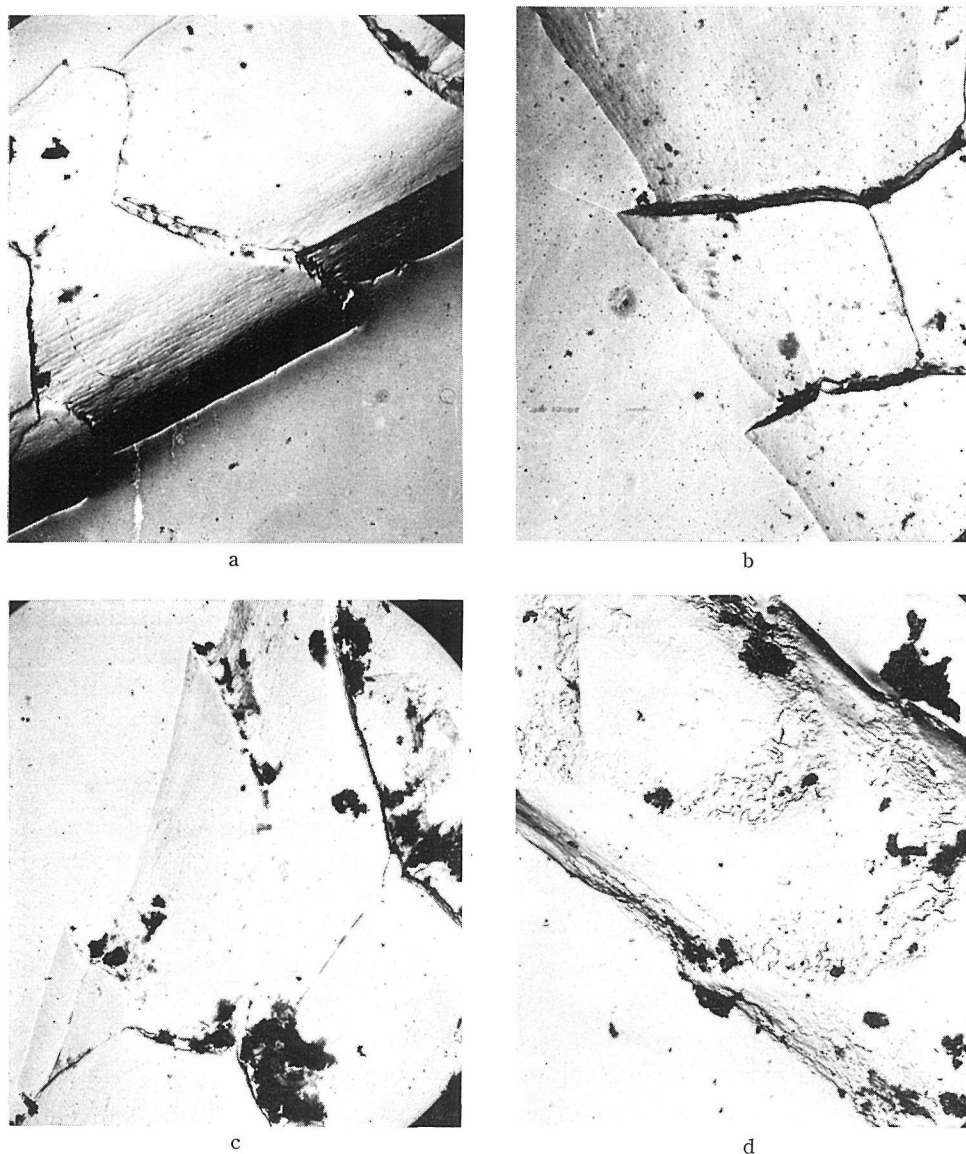


Fig. 2. Electron photomicrographs of the replicas of wool fiber specimen.
(a) Untreated. (b) Treated by the procedure of Type I. (c) Treated by the procedure of Type II. (d) Treated by the procedure of Type III.

X-ray Diffraction Patterns

The X-ray diffraction patterns of the fibers of the untreated wool and the wool treated by the procedures of Type I, II and III are schematically demonstrated in Fig. 3, a, b, c and d. The pattern of the fibers treated by the procedure of Type I, which is shown by Fig. 3, b, is apparently different from that of the untreated fibers, which is shown in Fig. 3, a. The reflection on the meridian, which would be due to the "folding spacing" disappears when the fibers are treated by the procedure of Type I. This suggests that the

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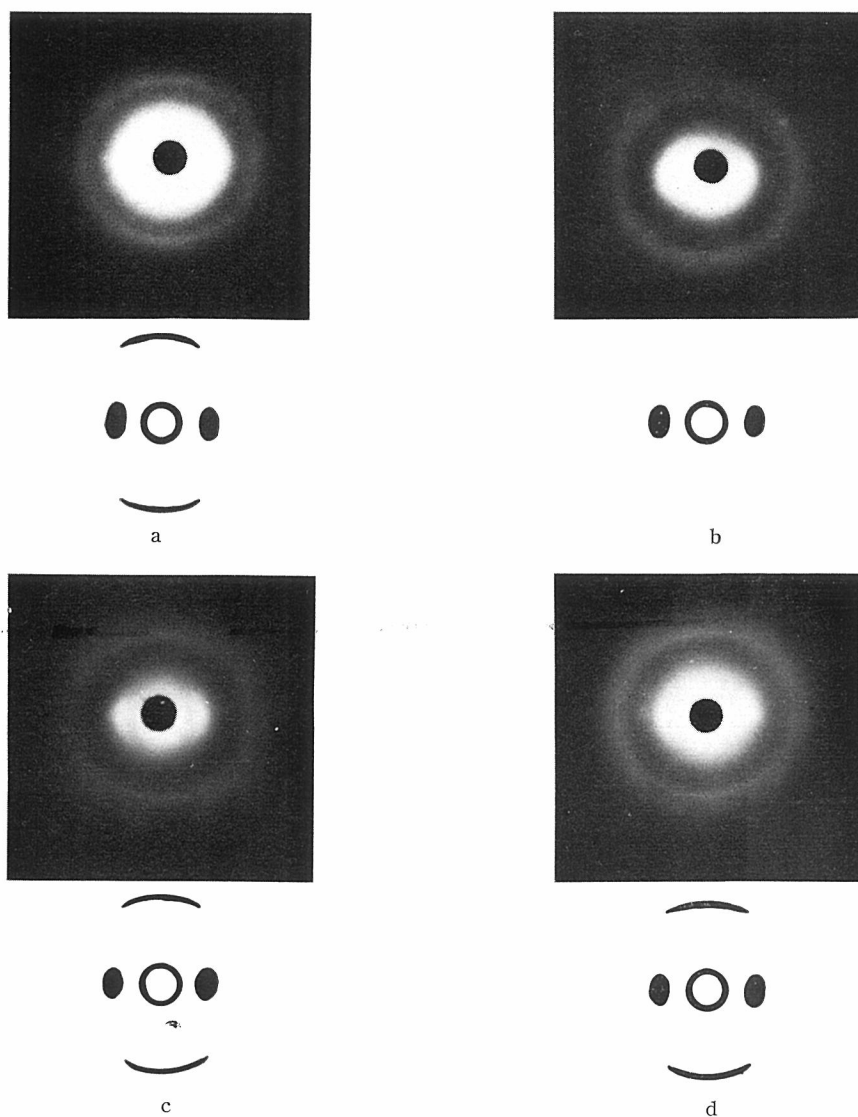


Fig. 3. X-ray diffraction patterns of wool fiber specimens.
 (a) Untreated. (b) Treated with the procedure of Type I.
 (c) Treated with the procedure of Type II. (d) Treated
 with the procedure of Type III.

chemical reactions of diisocyanate with the keratin molecules would result in the disturbance of the regularity along the polypeptide chain. The definite explanation cannot be given for the present, but it may be assumed that cross-links would be made by toluene diisocyanate within a folded chain, since the size of molecule of toluene diisocyanate is the magnitude which permits it. On the other hand, the molecule of toluene diisocyanate is too small to make cross-links between the polypeptide chains, and therefore, the backbone spacing and the side chain spacing are not affected.

The diffraction pattern remains almost unchanged at the treatment of Types II and III. This is natural, because the deposition of resin upon the wool surface is the main reaction of these two types of treatments.

TDI-ETHYLENE DIAMINE TREATMENT

The preliminary experiments revealed that the application of interfacial polymerization upon wool was most successful for securing the fabric and yarn stability, and that the employment of ethylene diamine (hereafter EDA) instead of other diamines so far used for interfacial formation of polyurea upon wool resulted in realizing the best effect. This induced us to study further in detail on the influence of conditions of the treatment upon yarn and fabric stabilization.

Samples

The same knit yarn as used in the previous experiments and the commercial wool blanket were employed. These commercial goods were thoroughly extracted by the mixture of methanol-benzene 1:1 in volume, washed with water and dried. 2 g. of the sample yarn was used for each experiment. For the experiments with the blanket a swatch having the dimension of 150×150 mm. was used each time.

Procedure

The sample yarn or blanket was dried and weighed, and immersed in the solution of TDI in a non-aqueous solvent, and squeezed by rolls so that the solution uptake was 100%. The wet sample was immersed in an aqueous solution of EDA for a certain time, washed with methanol, then with water to remove the reagents completely, and dried, and weighed. The uptake was expressed by the increase of weight in %. The concentration of TDI and EDA, and the time and temperature of immersion of sample in EDA solution were varied, and the influence of these conditions upon the uptake of resin was examined. The effect of solvent upon the uptake was studied by comparing the results obtained with carbon tetrachloride and toluene as the solvent of TDI. The sequence of treatment was changed, that is — the sample was first immersed in the aqueous solution, squeezed, and then in the non-aqueous solution. The uptake was almost the same as that of the ordinary order, but the reverse of the order resulted in making the TDI-solution turbid, possibly by the introduction of excessive water into the hydrophobic medium. Therefore, the order as mentioned first was employed in this study.

The Effect of Concentration of TDI

As can be readily expected, the uptake of resin increases almost linearly with the increase in the concentration of TDI, so far as other conditions are the same. The result is shown in Fig. 4. It is interesting to note that the uptake is greater when toluene is used as a solvent of TDI than it is when carbon tetrachloride is used. The length of time of immersion in the TDI

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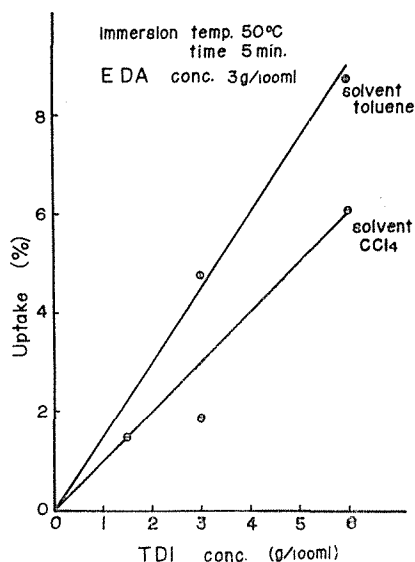


Fig. 4. Uptake of resin as a function of the concentration of toluene diisocyanate.

solution, and the temperature of the solution had only little effect upon the uptake of resin, so far as the sample was squeezed up to a definite ratio of the solution to the wool.

The Effect of Temperature of EDA Solution and Time of Immersion

Even if the absorption of TDI solution is the same, the amount of resin which is formed on the surface of fibers would depend upon the duration of immersion of the fibers in the EDA solution and the temperature at which the polymerization takes place. Fig. 5 shows the effect of temperature of EDA solution upon the uptake, and Fig. 6 the effect of the time of immersion

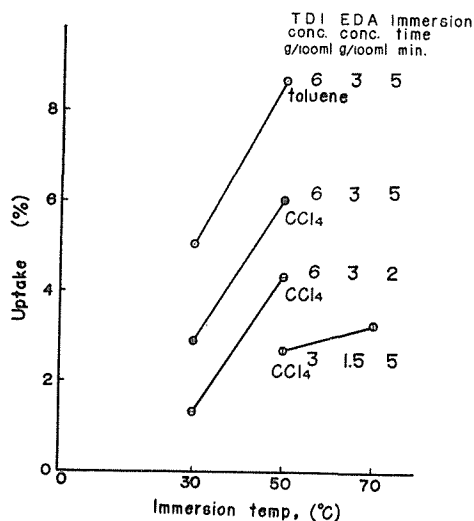


Fig. 5. Uptake as a function of the temperature of ethylene diamine solution.

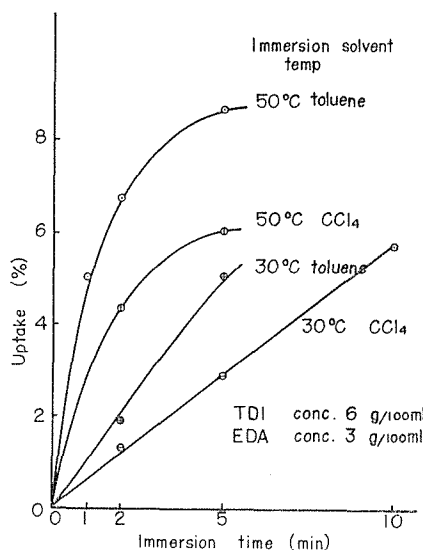


Fig. 6. Influence of the time of immersion in ethylene diamine solution upon the uptake of resin.

upon the uptake. The higher the temperature of reaction, the greater is the uptake, which, furthermore, increases with the time of immersion.

The Effect of Solvent

As can be deduced from the previous experiments, the solvent of the diisocyanate has a great influence upon the uptake of the resin. In every case, the uptake is greater when toluene is employed than it is when carbon tetrachloride is used. The difference between the uptakes in both the cases

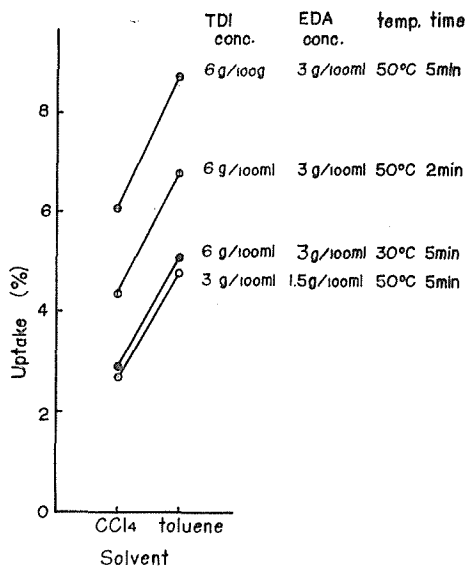


Fig. 7. Influence of the solvent of toluene diisocyanate upon uptake.

is demonstrated in Fig. 7. This would be due to the difference in the interfacial condition between the aqueous phase and non-aqueous phase, and the difference in the degree of swelling of wool in both the media.

The Relation between the Uptake and Shrinkage of Yarn

All the sample yarns which had been treated by the procedure of interfacial polymerization using TDI and EDA as reagents under various conditions as mentioned above were subjected to the shrinkage tests. Fig. 8 shows the

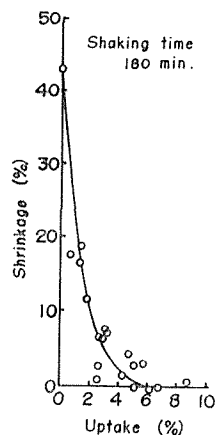


Fig. 8. Decrease in shrinkage as a function of uptake of resin.

plots of shrinkage after 180 min. of shaking vs. uptake. With the increase in uptake the shrinkage decreases, but the reduction at a definite uptake seems to be dependent upon the condition of treatment, because the plotted points considerably scatter. It can be deduced from the experiments that the shortening of time of immersion in EDA solution by elevating the temperature is effective to produce a higher stabilization effect at the same uptake. The employment of toluene is better than the use of carbon tetrachloride.

On the whole, however, the uptake of about 2% is enough to reduce the felting shrinkage up to below 10%. When the uptake is 5 to 6%, the shrinkage is practically at zero, but the yarn becomes harsher. The value from 2 to 5% may be recommended as an extent of uptake suitable in practice.

Experiments with Blanket

The swatch of blanket was treated in the same manner as in the case of knit yarn, and subjected to the shrinkage test. Toluene was used as the solvent of TDI. The temperature of the EDA bath was 50°C, and the time of immersion in this bath was 5 min. Before subjecting the swatch to the shrinkage test, the marks were sewed on the swatch so as to indicate the four corners of 120×120 mm. square. The swatch was stirred vigorously in 1.5% soap solution for 30 min. in a home laundry machine, and rinsed with water and dried. The distances between the sewed marks were measured, and the area shrinkage of the blanket was calculated. The results are shown

Table 2. Shrinkage tests of blanket processed by TDI-EDA treatment.

Sample	Concentration of TDI in %	Concentration of EDA in %	Uptake in %	Area shrinkage in %
Untreated	—	—	—	15.2
A	6.0	3.0	5.15	1.18
B	3.0	1.5	3.12	0.78

in Table 2. In this case also the uptake of polyurea resin from 2 to 5% is sufficient to make the blanket practically unshrinkable.

The Mechanical Properties of Single fibers

The single fibers were taken out carefully from the untreated and the treated yarns, and the load-elongation curve was measured for each single fiber. The load and elongation at break and the modulus of elasticity estimated from the initial slope of the load-elongation curve are tabulated in Table 3. The figures in the table represent the mean value respectively of

Table 3. The mechanical properties of single fibers.

Sample	Uptake in %	Load at break in g.	Elongation at break in %	Modulus of elasticity in kg/cm ²
Untreated	—	4.41	54.5	104
A	1.82	5.22	51.2	136
B	3.87	5.15	54.7	142
C	4.74	4.39	53.7	120
D	9.90	3.98	52.3	115

thirty measurements. This number of measurements is apparently too small, but the mean values thus obtained would serve for indicating the rough trend of change in mechanical properties of single fibers. The survey of the figures in Table 3 indicates that no prominent change in mechanical properties of single fibers is produced by applying the process of interfacial polymerization upon wool.

Moisture Regain

The absorption of moisture by fibers is one of the important character of wool from the practical point of view, and therefore, the equilibrium moisture contents at various relative humidities of the wool samples treated by the interfacial polymerization procedure were measured and compared with those of the untreated wool sample. The moisture regain was measured by placing the samples in a desiccator having a definite relative humidity for a sufficiently long period of time, until the equilibrium of moisture uptake is reached, and determining the weight at the equilibrium and the bone-dry weight of the sample. The result is given in Table 4, which indicates that the hygroscopic character of wool is not significantly modified by the treatment of

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Table 4. Moisture contents at various relative humidities.

Sample	Uptake in %	Moisture contents at various RH's in %				
		RH 16.7%	RH 35.4%	RH 56.7%	RH 79.4%	RH 87.4%
Untreated	—	5.33	8.26	10.59	14.20	18.38
A	0.6	5.00	8.33	11.28	15.15	19.45
B	1.8	5.02	7.95	10.80	14.45	19.54
C	3.9	4.96	8.03	10.69	14.70	18.75
D	4.7	5.08	7.95	10.67	14.81	18.80
E	9.9	4.63	7.57	10.25	14.13	18.40

interfacial polymerization method. This suggests that the layer of resin masking the surface of the fiber is permeable against moisture.

Frictional Behavior

As mentioned before, the decrease in the felting shrinkage of the yarns and fabrics treated by the present procedure depositing polyurea resin upon wool by the technique of interfacial polymerization is thought to be due chiefly to the change in the frictional behavior of individual fibers. The similar thing has been demonstrated by us (11, 12) in the studies on the shrinkproofing of wool by permanganate/sodium chloride treatment by measuring the coefficient of friction between a fiber and a mass of fibers of the same kind in a wet state. The fibers treated by the present procedure were also subjected to the measurement of frictional behavior under the same condition as that used in the previous studies (11, 12). The anti-scale coefficient of friction μ_1 , and the with-scale coefficient μ_2 , and the directional frictional effect given by the difference between both the coefficients, that is— $\mu_1 - \mu_2$, of the untreated fibers and treated fibers are shown in Table 5.

Table 5. Coefficients of friction and directional effect of fibers.

Sample	Uptake in %	Anti-scale coefficient of friction	With-scale coefficient of friction	Directional frictional effect
		μ_1	μ_2	$\mu_1 - \mu_2$
Untreated	—	0.53	0.19	0.34
A	0.6	0.47	0.23	0.24
B	4.7	0.47	0.30	0.17

It can be seen from the results that the with-scale coefficient increases, and the anti-scale coefficient decreases by the treatment, and eventually, the directional effect decreases by the treatment. This is the same as in the case of shrinkproofing by the potassium permanganat/sodium chloride treatment. In the latter case the fiber is smoothed by the chemical etching of the scale edges, whilst in the present case the fiber surface is smoothed by covering it with a uniform layer of polyurea resin.

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